

PRV

PATENT- OCH REGISTRERINGSVERKET
Patentavdelningen

PCT/ SE 03 / 0 1 0 4 9

REC'D 08 JUL 2003

WIPO PCT

Intyg Certificate

Härmed intygas att bifogade kopior överensstämmer med de handlingar som ursprungligen ingivits till Patent- och registreringsverket i nedannämnda ansökan.

This is to certify that the annexed is a true copy of the documents as originally filed with the Patent- and Registration Office in connection with the following patent application.

(71) Sökande Akzo Nobel NV, SB Arnhem NL
Applicant (s)

(21) Patentansökningsnummer 0202100-4
Patent application number

(86) Ingivningsdatum 2002-07-04
Date of filing

Stockholm, 2003-06-24

För Patent- och registreringsverket
For the Patent- and Registration Office

Sonia André
Sonia André

Avgift
Fee

PRIORITY DOCUMENT

SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)

Ink. t. Patent- och reg.verket

2002-07-04

Huvudfoxen Kassan

1

**AN ALKOXYLATE MIXTURE AND ITS USE AS A CLEANING AGENT
FOR HARD SURFACES**

5 The present invention relates to an alkoxybate mixture
of 2-ethylhexanol produced by first propoxylating and then
ethoxylating 2-ethylhexanol. The alkoxybate mixture has a low
content of unreacted 2-ethylhexanol and contains normally
between 2-20% of unethoxylated product. The alkoxybate
mixture is a good cleaning surfactant and wetting agent and
10 is also readily biodegradable.

2-Ethylhexanol is a suitable hydrophobic starting
material for production of surfactants, especially nonionic
alkoxylates, since it is low priced and readily available.
Thus, ethoxylated 2-ethylhexanol with a low amount of
15 unreacted alcohol is known from EP 845449 A1 to be a good
surfactant for the cleaning of hard surfaces, and it is also
readily biodegradable. According to this publication the
amount of unreacted 2-ethylhexanol must be kept very low and
this is achieved by using a narrow range catalyst for the
20 ethoxylation reaction normally followed by a distillation of
the ethoxylated product to remove the unreacted 2-
ethylhexanol.

EP 681 865 B1 describes wetting agents consisting of
mixtures of alkoxyated products, including products that
25 have been first propoxylated and then ethoxylated, but where
said mixtures always contain 30-60% of a propoxylated
product. There are examples of products based on 2-
ethylhexanol, but these are only pure propoxylates with 2, 6
or 10 PO units and also an alkoxybate with 8 PO and 6 EO
units per 2-ethylhexyl group. However, the alkoxybate is not
30 readily biodegradable.

In DE 42 12 592 A1 alkoxyates of PO and EO that are
low-foaming wetting agents with foam-inhibiting properties
are disclosed. However, 2-ethylhexanol is not mentioned as a
35 suitable basis for such alkoxyates.

In EP 652 281 A1 an alkaline aqueous composition comprising nonionic surfactants that are propylene oxide-ethylene oxide derivatives of an alcohol with a linear or branched alkyl or alkenyl group and 2.5-7 moles of PO and 1-10 moles of EO per mole alcohol is described. The alkyl group contains 4-11 carbon atoms. This composition is used for the cleaning of the surface of articles such as fruit, vegetables or containers for food, or for chemical peeling of fruit or vegetables, metal working or cotton mercerization. None of the examples relates to any product based on 2-ethylhexanol, and the amount of PO in the products displayed in the examples is 4-7 PO. The high amount of PO is a disadvantage because of the poorer biodegradability of such products as compared to the products with less PO.

Similar alkoxyates are also disclosed in US 4 965 014 and EP 34 194 B1, but in these publications the alkoxyates are only exemplified by products with predominantly longer alkyl chains.

The object of the present invention is to provide an alkoxyated product based on 2-ethylhexanol with an excellent combination of a good wetting ability, a low foaming, a good performance as a cleaning surfactant for hard surfaces and a good biodegradability and a low toxicity. Further, the product should be produced by a process that is simple to perform, and which is not too costly.

Now it has surprisingly been found that these objects are fulfilled by an alkoxyate mixture with the formula

$$C_6H_{13}CHCH_2O-(PO)_n-(EO)_m-H$$


where PO is a propyleneoxy unit, EO is an ethyleneoxy unit, n has an average value in the range 1.6 - 3.3, preferably 1.6-2.4 and most preferably 1.8-2.3, per 2-ethylhexyl group and m has an average value in the range 3.0-5.5, preferably 3.6-4.6, per 2-ethylhexyl group, and containing less than

1.5% by weight of unreacted 2-ethylhexanol; the said mixture being obtained by reacting 2-ethylhexanol in a first step with propylene oxide and in a second step the propoxylated mixture obtained with ethylene oxide.

5 The alkoxylate mixture has a very good cleaning and wetting ability, and is excellent for the cleaning of hard surfaces. It is readily biodegradable, exhibits a low toxicity towards fish, Daphnia and nitrifying bacteria and a moderate toxicity towards algae.

10 To obtain the excellent performance properties of the product, it is important to add and react all the propylene oxide in the first step, so that the PO-block is adjacent to the 2-ethylhexoxy group. The product resulting after the ethoxylation, which is performed in the second step, will
15 contain some unethoxylated product, i.e. 2-ethylhexanol that has only been propoxylated. Typically, this propoxylate will be present in an amount of between 2 and 20% by weight, normally between 5 and 15% by weight. The presence of propoxylates in the mixture improves the wetting ability and
20 reduces the foaming. The total amount of PO in relation to the 2-ethylhexanol is also important. If the amount is too low, the performance of the product will not be optimal, and if the amount of PO is too high, the biodegradability will be poorer. Also the balance between EO and PO is important for
25 the performance, and in an especially preferred embodiment the molar ratio EO/PO is in the range 1.6-2.6.

30 The alkoxylate mixture could be used in aqueous cleaning compositions together with other conventional components, such as alkali and/or alkaline complexing agents, hydrotropes, other surfactants, thickening agents, solvents, colourants, soil antiredeposition agents, defrosting stabilizers, preservatives, corrosion inhibitors and foam regulators.

35 The invention also relates to a method for producing the alkoxylate mixture, where 2-ethylhexanol is reacted with

1.6-3.3, preferably 1.6-2.4 and most preferably 1.8-2.3, moles of propylene oxide per mole 2-ethylhexanol in the presence of a propoxylation catalyst at a temperature from 110°C to 130°C in a first step where the total amount of propylene oxide is allowed to react, whereupon the propoxylate mixture obtained, or the propoxylate mixture resulting after removal of unreacted 2-ethylhexanol, is reacted in a second step with 3.0-5.5, preferably 3.6-4.6, moles of ethylene oxide per mole 2-ethylhexanol propoxylate in the presence of an ethoxylation catalyst at a temperature from 60°C to 180°C.

The propoxylation step can be performed in the presence of a propoxylation catalyst, preferably an alkaline catalyst selected from the group NaOH, KOH, NaOCH₃ and KOCH₃. For the ethoxylation step either an alkaline catalyst selected from the group NaOH, KOH, NaOCH₃ and KOCH₃, or a narrow range catalyst selected from the group Brönstedt acids, Lewis acids and Ca(OH)₂, could preferably be used. If a Brönstedt or Lewis acid is to be used in the ethoxylation step, the alkaline catalyst used in the first step should either be removed or neutralized before the start of the ethoxylation step. Preferably both the propoxylation and the ethoxylation step are performed in the presence of an alkaline catalyst, most preferably in the presence of KOCH₃.

The present invention is further illustrated by the following Examples.

Example 1

In Table 1 some properties for alkoxylate mixtures according to the invention and alkoxylates used for comparison are collected.

The wetting ability was measured according to the modified Drave's test, where the sinking time in s is measured for a specified cotton yarn in approximately 0.1% surfactant solution.

5 The foam was measured as mm foam produced in a 500 ml measuring cylinder with 49 mm inner diameter from 200 ml of 0.5g/l surfactant solution when the cylinder is turned around 40 times in one minute. The test was made at room temperature and the foam height was registered directly and after 1 minute.

10 For the test of cleaning efficiency a formulation in water containing 6% tetra potassium pyrophosphate, 4% sodium metasilicate x 5 H₂O, 5% alkoxylate and 2.4% sodium octyliminidipropionate was used. This formulation was diluted 1:30 with water.

Cleaning test procedure:

15 White painted plates were smeared with an oil-soot mixture obtained from diesel engines. 25 ml of the above-mentioned diluted formulation were poured onto the top of the oil-smeared plates and left there for one minute. The plates were then rinsed off with a rich flow of water. All solutions and the water were kept at a temperature of about 15-20°C. The cleaning efficiency was evaluated by measuring the amount of soil that had been removed from the surface, and where 100% represents a totally white and clean surface. The evaluation was performed by measuring the reflectance of the plates with a Minolta Chroma meter CR-200 reflectometer before and after the cleaning.

25 The amount of free 2-ethylhexanol in the alkoxylate mixture was determined by gas chromatography.

Table 1

Product	Wetting Sinking time (s)	Foam height (mm) after 0 and 1 min	Foam height ^d (mm) after 0 and 1 min	Cleaning efficiency % removal	Free alcohol in alkoxylate (%)
2-EH+2PO+ 4EO ¹	7	20/0	10/1	80	1.1
2-EH+2PO+ 4EO ²	12				0.4
2-EH+4EO ³	90	12/0	25/1	40	< 0.5
2-EH+4EO ⁴	125	37/0	70/20	20	11.4
2-EH+2PO+ 10EO	194	75/17			0.2
2-EH+3PO+ 10EO	100	84/8			0.1
2-EH+4PO+ 10EO	83	83/5			0.05
2-EH+4EO+ 2PO	61	8/0			1.7

2-EH = 2-ethylhexanol

¹alkaline catalyst used in both propoxylation and ethoxylation step5 ²alkaline catalyst used in propoxylation step and narrow range catalyst used in ethoxylation step³product produced according to EP 845 449 A1⁴alkaline catalyst used for ethoxylation^dFoam height obtained using the cleaning formulation above

10 From the results it is evident that the alkoxylate mixtures according to the invention have an excellent combination of good wetting ability, low foaming and high cleaning efficiency.

Example 2

In Table 2 toxicity data for alkoxyate mixtures according to the invention and alkoxyates used for comparison are collected.

- 5 The biodegradability test was performed according to OECD 301 B.

The following toxicity tests have been used:

Fish (*Oncorhynchus mykiss*): OECD 203

Algae (*Scenedesmus subspicatus*): OECD 201

- 10 *Daphnia magna*: OECD 202

Nitrifying bacteria: ISO guidelines (1989) No. 9509

The following results were obtained.

Table 2

Product	Biodegradability	Fish LC 50 (mg/l)	Algae EC50 (mg/l)	Daphnia EC50 (mg/l)	Nitrifying bacteria EC 50 (mg/l)
2-EH+2PO +4EO	> 60%	42	7	48	>1000
2-EH+ 4EO ¹	> 60%	13	6	7	680
2-EH+4PO +10EO	< 60%				

2-EH = 2-ethylhexanol

- 15 ¹product produced according to EP 845 449 A1

The alkoxyated mixture according to the invention is readily biodegradable, has a low toxicity towards fish and nitrifying bacteria and a moderate toxicity towards algae.

Example 3

- 20 48 kmol of 2-ethylhexanol and 2 $\frac{1}{2}$ by weight, based on the alcohol, of KOCH₃, were charged into an alkoxylation reactor. The reactor was rinsed with nitrogen gas, and methanol was evaporated. The reactor was evacuated, the temperature increased to 120°C and propylene oxide was charged in a total amount of 96 kmol. After completion of the reaction, the
- 25 temperature was raised to 160°C and ethylene oxide was

charged in a total amount of 192 kmol. The resulting product was neutralized with acetic acid.

Example 4

5 The same procedure as in Example 3 was followed, except that 1% by weight, based on the alcohol, of KOH was used for the propoxylation reaction, the intermediate propoxylate was neutralized and the ethoxylation step was performed at 70°C in the presence of 0.3% by weight of BF_3 , which is a catalyst that gives a narrow distribution of ethylene oxide units.

Ink. t. Patent- och reg.verket

7007 -07- 0 4

Huvudfaxen Kossan

9

C L A I M S

1. An alkoxyate mixture, characterized in that it has the formula



10 where PO is a propyleneoxy unit, EO is an ethyleneoxy unit, n has an average value in the range 1.6-3.3 per 2-ethylhexyl group and m has an average value in the range 3.0-5.5 per 2-ethylhexyl group, and containing less than 1.5% by weight of unreacted 2-ethylhexanol; the said mixture being obtained by reacting 2-ethylhexanol in a first step with propylene oxide and in a second step the propoxylated mixture obtained with
15 ethylene oxide.

2. Alkoxyate according to claim 1, characterized in that the amount of 2-ethylhexyl propoxyate is between 2 and 20% by weight.

3. Alkoxyate according to claim 1 or 2, characterized in
20 that n has an average value in the range 1.6-2.4 and m has an average value in the range 3.6-4.6.

4. Alkoxyate according to claim 1, 2 or 3, characterized in that n has an average value in the range 1.8-2.3 and m has an average value in the range 3.6-4.6.

25 5. Alkoxyate according to claim 1, 2, 3 or 4, characterized in that the molar ratio between ethylene oxide and propylene oxide is in the range 1.6-2.6.

6. Method of producing an alkoxyate mixture, characterized in that 2-ethylhexanol is reacted with 1.6-3.3 moles of
30 propylene oxide per mole 2-ethylhexanol in the presence of a propoxylation catalyst at a temperature from 110°C to 130°C in a first step where the total amount of propylene oxide is allowed to react, whereupon the propoxyate mixture obtained, or the propoxyate mixture resulting after removal of
35 unreacted 2-ethylhexanol, is reacted in a second step with

Ink. t. Patent- och reg.verket

2007-07-04

10

Huvudfaxen Kassar

3.0-5.5 moles of ethylene oxide per mole 2-ethylhexanol propoxylate in the presence of an ethoxylation catalyst at a temperature from 60°C to 180°C.

5 7. Method according to claim 6, characterized in that the propoxylation catalyst is an alkaline catalyst selected from the group NaOH, KOH, NaOCH₃, and KOCH₃.

10 8. Method according to claim 6 or 7 characterized in that the ethoxylation catalyst is an alkaline catalyst selected from the group NaOH, KOH, NaOCH₃, and KOCH₃, or a narrow range catalyst selected from the group Brönstedt acids, Lewis acids and Ca(OH)₂.

9. Method according to claim 7 or 8, characterised in that the propoxylation and ethoxylation catalyst is KOCH₃.

15 10. Use of the alkoxylate mixture according to any of claims 1 to 5 for the cleaning of hard surfaces.

ABSTRACT

The invention relates to an alkoxylate mixture having the formula



where PO is a propyleneoxy unit, EO is an ethyleneoxy unit, n has an average value in the range 1.6-3.3 per 2-ethylhexyl group and m has an average value in the range 3.0-5.5 per 2-ethylhexyl group, and containing less than 1.5% by weight of unreacted 2-ethylhexanol; the said mixture being obtained by reacting 2-ethylhexanol in a first step with propylene oxide and in a second step the propoxylated mixture obtained with ethylene oxide.

10

15

The alkoxylate mixture is a good cleaning surfactant and wetting agent and is also readily biodegradable.